PAPER • **OPEN ACCESS**

Electrochemical investigations of surfactants influence on copper ions cementation

To cite this article: E B Kolmachikhina *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **848** 012034

IOP Conf. Series: Materials Science and Engineering **848** (2020) 012034 doi:10.1088/1757-899X/848/1/012034

Electrochemical investigations of surfactants influence on copper ions cementation

E B Kolmachikhina[1*], E A Ryzhkova[1], D V Starkova[1] and V A Val'nev[1]

[1] Ural Federal University, 17, Mira St., Ekaterinburg, 620002, Russia
[*]Corresponding author: e.b.khazieva@urfu.ru

Abstract. The paper presents the results of experiments aimed to determine the effect of surfactants on the cementation rate and activation energy. The study was carried out on model solutions with the addition of surfactants. The results of the study showed that sodium lignosulfonate in a mixture with sodium dodecyl sulfate and sodium dodecylbenzene sulfonate increases the cementation rate over the entire range of studied concentrations. It is noted that the addition of individual surfactants leads to an increase in activation energy. Activation energy increases according to following order: sodium dodecylbenzene sulfonate → sodium dodecyl sulfate → sodium lignosulfonate.

1. Introduction

Cementation by zinc dust is widespread method for zinc solutions purification from ions of cobalt, copper and nickel. According to numerous investigations, organic impurities (incl. surfactants) have negative influence on cementation and zinc electrowinning results. Main cause of this phenomena is surfactants adsorption on zinc and copper particles [1,2]. Surfactant are used at pressure leaching of zinc sulfide concentrates to eliminate sulfur-sulfide pellets formation. Remaining surfactants in solution after leaching complicate further purification from ferrous and ferric ions, cementation purification from copper, cadmium, nickel and cobalt ions. Also surfactants could affect on results of zinc electrowinning.

Balkhash zinc plant (Kazakhstan) practices demonstrated that sodium lignosulfonate (SL) usage raises zinc extraction at leaching, but complicates cementation of solutions later on [3]. Presence of SL claims to enhance of zinc dust consumption at purification stages. SL significantly decreases degree of purification from cobalt and nickel ions [4].

Work results [5] confirm that presence of lignosulfonates degradation product leads to cementation velocity decreasing, zinc consumption increasing for copper ions reduction.

It was established [4, 6], that sodium dodecylsulfate (anionic surfactant), cetyl trimethylammonium bromide (cathionic surfactant) and Triton X-100 (nonionic surfactant) has negative influence of 32-94 % on copper cementation effectiveness.

Cementation purification in presence of organic reagents is complicated due to several reasons: decreasing of hydrogen overvoltage, organic impurities adsorption, stable complex compounds formation with metals ions and organic components.

The aim of this study is surfactants (SL, sodium dodecylsulfate (SDS), sodium dodecyl benzenesulfonate (SDBS) influence investigation on results of copper ions cementation.

2. Methods

Electrochemical investigations were carried out for cementation process tracking through current intensity movement during experiment.

For electrochemical investigations a model sulfate solution of 0.5 $g \cdot l^{-1}$ Cu^{2+} was used. Concentrations of SL, SDS and SDBS and their mixtures were varied from 50 to 400 $mg \cdot l^{-1}$. Experiments temperature was fixed at 25, 45, 65 ^oC. Mixing rate was 500 rpm.

Tests were carried out on electrochemical workstation «ZIVE SP2». Work electrode (cathode) was made from zinc rod with diameter 0.4 cm, subsidiary electrode – from lead thin plate, reference electrode – silver chloride electrode.

Experiments were conducted under constant potential (0 V vs SCE). Solutions after experiments were analyzed on copper concentration by atomic absorption spectrometry (Analytik Jena, NovAA 300).

Cementation velocity was estimated through copper concentration (1) and current changing (Faraday's laws of electrolysis).

$$W=\frac{(C_0-C_t)\cdot V}{t\cdot S}, \quad (1)$$

W – specific cementation velocity, $g \cdot cm^{-2} \cdot s^{-1}$;
V – solution volume, l;
C_o – initial copper concentration, $g \cdot l^{-1}$;
C_t – copper concentration at time t, $g \cdot l^{-1}$;
t – test duration, s;
S – disc area, cm^2.

3. Experiments results and discussions

Using STATISTICA software obtained results were presented as three-dimensional graph characteristic of cementation velocity from temperature and surfactants concentrations (figures 1-3).

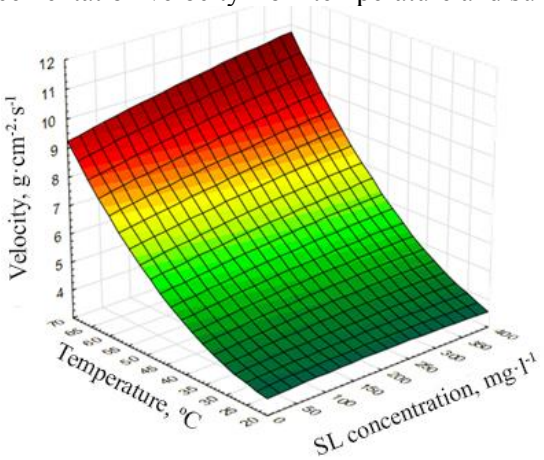

Figure 1. Dependence of copper cementation velocity from temperature and SL concentration

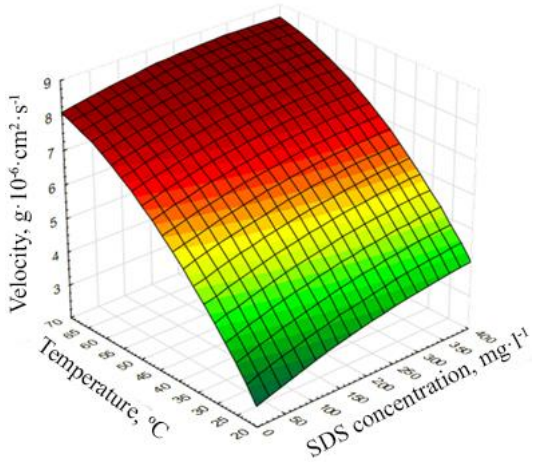

Figure 2. Dependence of copper cementation velocity from temperature and SDS concentration

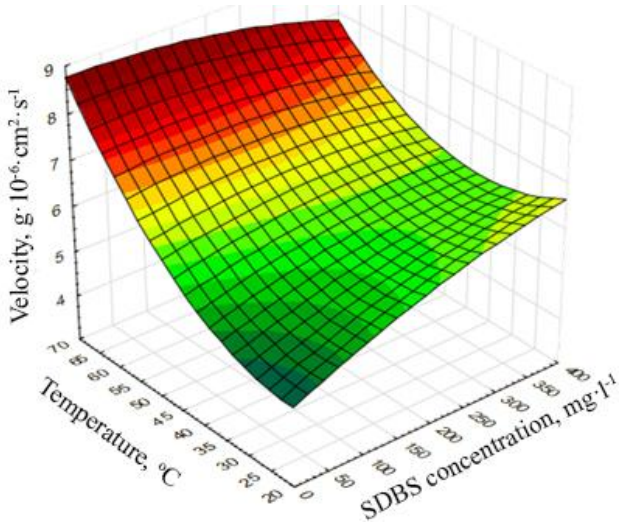

Figure 3. Dependence of copper cementation velocity from temperature and SDBS concentration

Obtained results testify that at 25 °C copper cementation velocity decreases from $4.06 \cdot 10^{-6}$, $g \cdot cm^{-2} \cdot s^{-1}$ without surfactants to ~$3.7 \cdot 10^{-6}$ $g \cdot cm^{-2} \cdot s^{-1}$ at all SL concentrations. However, at elevated temperature process rate increases from $5.24 \cdot 10^{-6}$ $g \cdot cm^{-2} \cdot s^{-1}$ to $6.01 \cdot 10^{-6}$ $g \cdot cm^{-2} \cdot s^{-1}$ at 45 °C and from $8.40 \cdot 10^{-6}$ $g \cdot cm^{-2} \cdot s^{-1}$ to $9.45 \cdot 10^{-6}$ $g \cdot cm^{-2} \cdot s^{-1}$ at 65 °C in absence and presence of 400 $mg \cdot l^{-1}$ SL, respectively.

SDS and SDBS usage at 25 °C and 45 °C leads to cementation velocity increasing. At SDS addition velocity increases at 25 °C and 45 °C on 21.8 % and on 31.6 %, respectively; at SDBS rate increases on 52.6 % and 24.6 % at 25 °C and 45 °C, respectively. However, SDBS at 65 °C leads to decreasing of copper cementation rate.

Also surfactant mixes influence was investigated, surfactants concentrations were in range from 50 to 400 $mg \cdot l^{-1}$ at 65 °C (figures 4, 5).

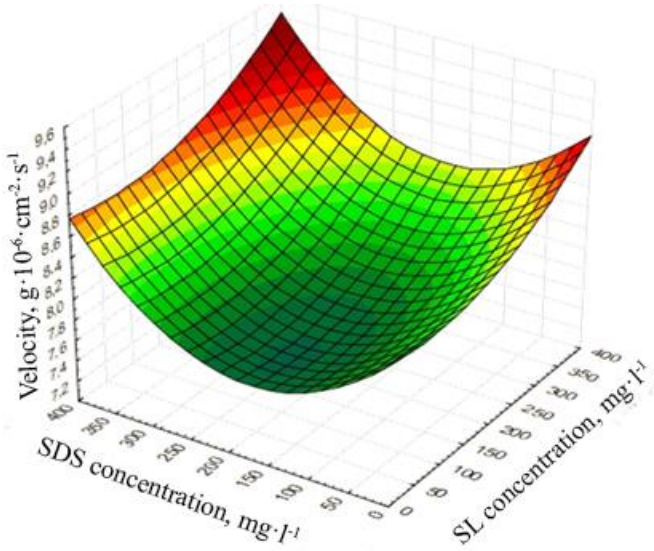

Figure 4. Cementation velocity dependence on LS and SDS concentrations

LS in mixes with SDS leads to cementation rate increasing at all range of studied concentrations. In some cases, the rates were lower than at surfactants absence ($8.40 \cdot 10^{-6}$ g·cm^{-2}·s^{-1}). Maximum rates were observed in presence of mixes of LS 50 mg·l^{-1}+SDS 400 mg·l^{-1} ($8.64 \cdot 10^{-6}$ g·cm^{-2}·s^{-1}), LS 200 mg·l^{-1}+SDS 400 mg·l^{-1} ($8.87 \cdot 10^{-6}$ g·cm^{-2}·s^{-1}), LS 400 mg·l^{-1}+SDS 200 mg·l^{-1} ($8.92 \cdot 10^{-6}$ g·cm^{-2}·s^{-1}), LS 400 mg·l^{-1}+SDS 400 mg·l^{-1} ($9.42 \cdot 10^{-6}$ g·cm^{-2}·s^{-1}) at 65 ºC.

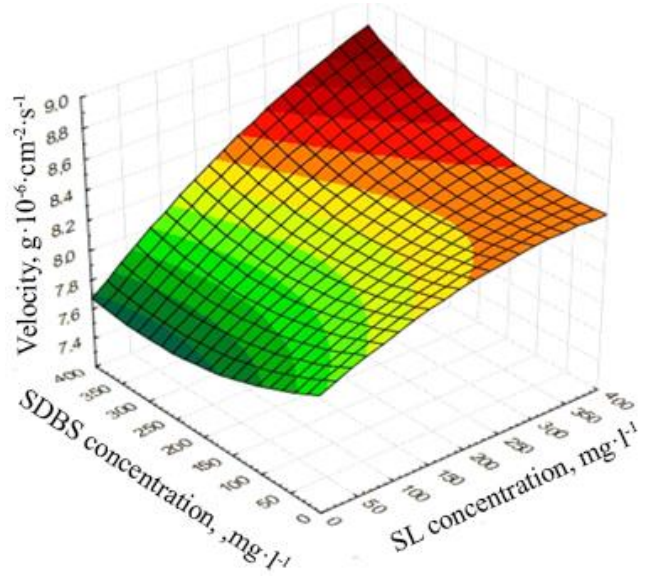

Figure 5. Cementation rate dependence on SL and SDBS concentration

It was established that SDBS with SL increases copper reduction rate at surfactants concentration enhancing. At low SL concentrations (50 mg·l^{-1}) cementation rate was lower than at surfactants absence. At the same time, in case of SL usage (200, 400 mg·l^{-1}) it was marked a slight rate increasing up to 4 %.

Experimental rate constant was estimated by followed equation (2):

$$K_e = \frac{W_{av}}{S \cdot C_t \cdot n^{0.5}}, \quad (2)$$

Ke – experimental rate constant;

Wav – average cementation rate, mole·cm^{-2}·s^{-1};

S – disk area, cm^2;
Ct – copper concentration, $mole \cdot l^{-1}$;
n – disk rotation speed, rounds per second.

Energy of activation estimations were carried out by Arrhenius equation in logarithmical form (lgKe – 1/T). At figure 6 dependence of - lgKe on reciprocal temperature in SL presence is shown. analogous dependences were built for SDS, SDBS and their mixes with SL.

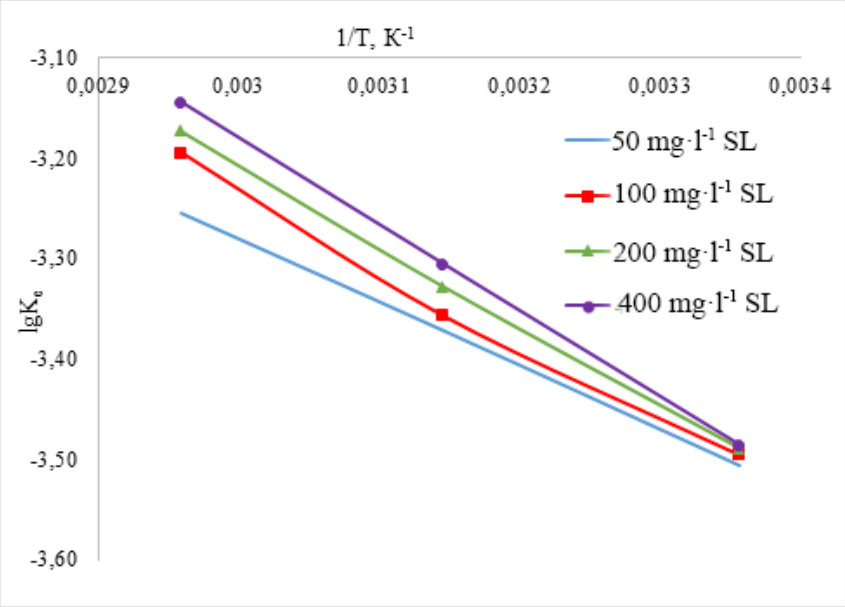

Figure 6. Dependence of - lgK_e on 1/T in SL presence

Addition of surfactants led to activation energy enhancing in the order SDBS→SDS→SL (figure 7). After achievement of 200 $mg \cdot l^{-1}$ of any surfactants an activation energy remains at a plateau, that could be related with reagents adsorption monolayer formation. Such effect was observed at surfactants mixes addition. Maximum activation energy was at SL addition (16.49 $kJ \cdot mole^{-1}$), at SDS usage – 11.23 $kJ \cdot mole^{-1}$, at SDBS – 10.84 $kJ \cdot mole^{-1}$.

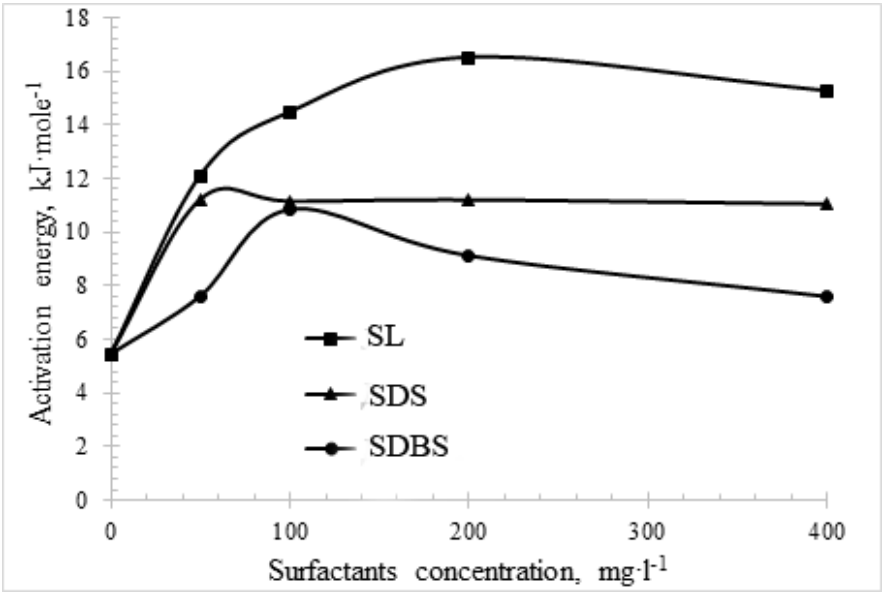

Figure 7. Activation energy dependence on surfactants concentration

Such influence was noted with all used mixtures: the higher SL concentration, the higher activation energy. Comparably with SL addition while using mixes remarkable activation energy increasing was observed: SL 50 mg·l^{-1}+SDS 200 mg·l^{-1} on 34.5 %, SL 200 mg·l^{-1}+SDS 200 mg·l^{-1} on 24.2 %, SL 400 mg·l^{-1}+SDS 200 mg·l^{-1} on 38 % (figure 8). While using of SL and SDBS mixes it was shown that there is an additive effect of reagents on energy activation growth (figure 9).

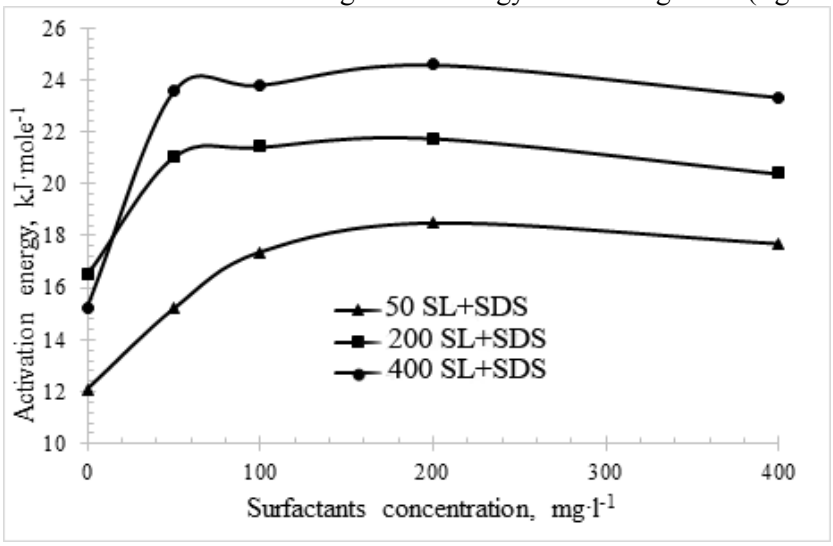

Figure 8. Activation energy dependence on concentration of SL and SDS mixes

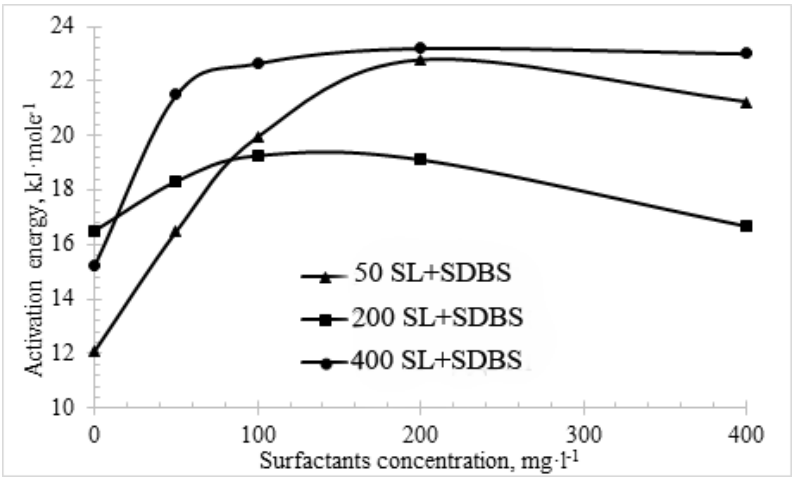

Figure 9. Energy activation energy on concentrations of SL and SDBS mixes

Energy activation increasing at SL usage could be associated with participating of SL function groups in donor-acceptor interactions with metal ions that leads to formation of complexes with Cu^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+} by means of sulfonate groups and phenolic hydroxyl groups [7]. At complexes formation activation energy increases due to stronger chemical bonding and it needs more energy for their breaking.

4. Conclusion

1. Surfactants addition (SDS, SDBS, SL) at 45 ºC don't lead to copper cementation velocity decreasing;
2. Mixes of SL+SDS, SL+SDBS increases of cementation velocity;
3. Surfactant addition increases activation energy: SDBS→SDS→SL;
4. Surfactants concentration increasing up to 200 mg·l^{-1} leads to energy activation enhancing.

Acknowledgment
Leaching experiments and grade size analysis were conducted at the expense of the Russian Science Foundation grant (project No. 18-19-00186).

References
[1] Karavasteva M 1997 *Hydrometallurgy* **3** 91-98
[2] Demeev B B, Dauletbay A, Nauryzbaiev M K 2016 *Chemical Engineering Transactions* **47** 211-216
[3] Piskunov V M 2006 *Sbornik nauchnykh trudov VNIITCVETMETa* 56-58
[4] Drweesh M A 2004 *Alexandria Engineering Journal* **6** 917-925
[5] Khazieva E B, Naboichenko S S, Bolatbaev K N 2015 *Russian Journal of Non-Ferrous Metals* **56** 142-145
[6] Abdel-Aziz M H 2011 *Hydrometallurgy* **109** 161-167
[7] Khvan A M 1990 *Chemistry of Natural Compounds* **26** 575-577